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THE RATIO OF THE CALORIE AT 73° TO THAT AT 20°.

By Arnold Romberg.

Investigations on Light and Heat made and published with aid from the Rumford Fund.

(Continued from page 3 of cover.)

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The present paper, publication of which has been deferred for various reasons, describes an experiment designed as a crucial test of the correctness of the temperature variation curve of the specific heat of water. The desirability of such a test is apparent from figure 1,

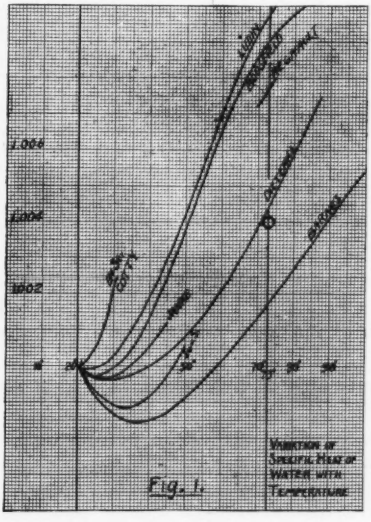

Fig. 1.

which gives the results of some of the best researches on the subject, and which shows the great discrepancies existing at the higher temperatures.[1] The work was suggested by H. N. Davis, and carried out in

[1] The task of finding from the published papers the reasons for the differences in these curves must be regarded as hopeless. In connection with the excellent work of Barnes a possible source of error may however be pointed out. The heating current in Barnes's calorimeter is carried by a platinum wire between copper terminals at which a certain amount of heat is absorbed and liberated, respectively, due to the Peltier effect. The thermometers are situated within these hollow terminals, and it is conceivable that an appreciable error might result.

the Jefferson Physical Laboratory of Harvard University, and to Professor Davis is also due the distinctive feature of the method, as will be pointed out below.

The method may be explained schematically by reference to the diagram, figure 2. Hot water flows through a tube F_1 containing resistance thermometers T_1 and T'_1, the tube being in thermal contact at C between these two points, with another similar system F_2, in which cold water is flowing. The two streams of water are made equal. The thermal coupling C is variable; a device due to Professor Davis, and of fundamental importance in giving the method its advantage.

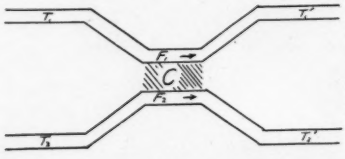

Fig. 2.

With constant temperatures T_1, T_2, and flow f, readings are taken of $T_1 - T'_1$ or $T'_2 - T_2$, and of $(T_1 - T'_1) - (T'_2 - T_2)$. This is repeated for other values of the flow, and for other conditions of the thermal coupling.

If there are no complications, and if $T_1 - T'_1$ is small, the ratio of the specific heats is

$$\frac{c_1}{c_2} = \frac{T'_2 - T_2}{T_1 - T'_1}$$

and therefore

$$\frac{c_2 - c_1}{c_2} = \frac{(T_1 - T'_1) - (T'_2 - T_2)}{T_1 - T'_1} = \frac{\Delta_0}{\Delta_1}$$

Heat currents to and from the flowing stream at places other than C may introduce errors in the thermometer readings. These errors may be represented as

1) $\partial_1 t = \dfrac{A(T_1, T_2)}{f}$ Depending upon the temperature variations of the water-supply.

2) $\partial_2 t = \dfrac{B\Delta_1}{f}$ Due to cross-heat-losses proportional to the temperature differences $T_1 - T'_1$ and $T_2 - T'_2$.

3) $\partial_3 t = C(f, i)$ Due to differences in the temperature rise produced by the thermometric measuring current in the different (resistance-) thermometers.

4) $\partial_4 t = W(f)$ Due to the heat-equivalent of the work of forcing the water through the tubes.

These errors will influence the quantity $\Delta_0 = (T_1 - T'_1) - (T'_2 - T_2)$ by an amount

$$\partial t = \partial_1 t + \partial_2 t + \partial_3 t + \partial_4 t = \frac{A + B\Delta_1}{f} + C + W$$

The true value of $(c_2 - c_1)/c_2$ in terms of the flow and the measured temperatures is therefore

$$\frac{c_2 - c_1}{c_2} = \frac{\Delta_0 + \partial t}{\Delta_1} = \frac{\Delta_0}{\Delta_1} + \frac{1}{\Delta_1}\left[\left(\frac{A + B\Delta_1}{f}\right) + C + W\right]$$

from which

$$\Delta_0 = \left(\frac{c_2 - c_1}{c_2} - \frac{B}{f}\right)\Delta_1 - \frac{A}{f} - C - W$$

If Δ_0 and Δ_1 be regarded as variables, this equation represents a family of straight lines of slope

$$p = \frac{c_2 - c_1}{c_2} - \frac{B}{f}$$

from which $(c_2 - c_1)/c_2$ may be obtained by varying the parameter f. If B is small, f need not be accurately known (in the work to be described the B/f correction was of the order of .001). The ratio $(c_2 - c_1)/c_2$ has been assumed constant over the range of temperatures employed. This assumption, not hazardous in the first place, is experimentally justified if the data for any one flow lie on a straight line. That this was true within the limits of error of the data presented below, appeared from the preliminary tests.

The temperatures T_1 and T_2, which are not changed, have no influence on the changes in Δ_1 or Δ_0, and are mere auxiliary temperatures. The thermometers at these temperatures serve only to balance the bridge, and to compensate automatically for any slight changes that might occur in the water supply temperatures.

The measurement of the changes in $\Delta_1 = T_1 - T'_1$, or $\Delta_2 = T'_2 - T_2$, by determining the difference $R_1 - R'_1$, or $R'_2 - R_2$ between a pair of similar thermometers, to the required accuracy of one per cent, is not

difficult, and need not be discussed. The value of Δ_0 or $(T_1 - T'_1) - (T'_2 - T_2)$ is measured as $(R_1 - R'_1) - (R'_2 - R_2)$ on a Carey Foster bridge. The changes in Δ_0 thus measured are in terms of a temperature scale defined by R'_1 and R'_2 in their respective temperature regions. They may be subsequently expressed in terms of a single one of the thermometers used, and finally reduced to the gas scale by comparing this thermometer with one that has been tested for its "delta." These reductions involve a determination of the differences between the temperature coefficients of the thermometers T_1 and T_2, and between one of them and T_3, the thermometer whose "delta" is known. There is no need of accurate knowledge of the resistance of any thermometer in any unit, nor of the relative resistance of any pair of them, nor of their temperature coefficients. Nowhere in the work is there any need of knowledge of the heat loss, of the heat capacity of the apparatus, or of the work of the flowing water. No absolute precision measurement is required in the entire calorimetric work, and but a single such measurement, that of the Callendar "delta" of one of the thermometers, in the entire work.

The apparatus may best be described by following the course of the water through it. Water enters at A (see Fig. 3) from a regulating valve from which it flows under a head of about eight inches, kept constant by an overflow. It flows into a steam heater B, where it boils. An arrangement not shown allows air to escape from the top of this heater. The water is then cooled to about 80° by a cold water circulation, and enters a coil of about 100 feet of 3/8″ copper tubing in the hot thermostat, where it is brought to the inflow temperature — usually 78°. This temperature is kept constant by a regulator not shown, which will be described later. From the thermostat the water enters the thermometer tube T_1, which is lagged with wool, and is placed in a 4″ tube jacketed by the thermostat itself. It then passes through a Dewar tube D, and a straight glass tube, into one of the copper tubes of the thermal coupling, which consists of two tubes coiled together in a double layer, in such a manner that the hot water flows in alternate turns of each layer. It then passes up in tubes D'_1 and T'_1 situated behind D_1 and T_1, and passes a second thermometer inside the same jacketing tube. It then passes to the cooler, where a tap-water circulation brings it to a temperature of about 12°. It then traverses the cold thermostat coil, where it is brought to about 16°; then the thermometer tube T_2, etc., and takes up in passing through the second tube of the coupling a quantity of heat which may be controlled by varying the amount of mercury in the bottom of the Dewar

flask protecting the coupling. Finally it flows out through the fourth thermometer tube, to a pump which returns it to the constant-head reservoir above *A*. Distilled water is used, and renewed from time to time.

It was intended to choose the temperature so that the ratio of the 75° calorie to the 20° calorie might be obtained. The actual temperatures chosen happened to be somewhat more easily handled with the thermostats.

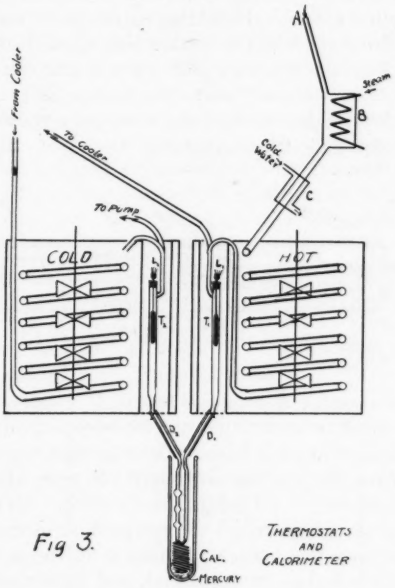

Fig 3.

The resistance thermometers contain about 33 ohms of No. 42 platinum wire, coiled in helixes of inside diameter .02″, silver-soldered to copper leads, which are passed in the shape of ribbon $\frac{1}{4}$″ wide between copper leaves of somewhat greater width, and $2\frac{1}{2}$″ long, from which they are insulated by mica. They are held between these leaves by a tight winding of copper ribbon. The purpose of this arrangement is to make certain that the leads come to the temperature of the thermometer case, and to this end the copper leaves referred to are silver-

soldered into saw-cuts in the copper plug which joins the two parts of the case. Compensating leads, carrying about $\frac{1}{2}$ ohm of platinum, are provided. Figure 4 shows the thermometer somewhat distorted, the upper portion being drawn too short. These thermometers show a temperature rise of .02 degrees with the measuring current of 3 milliamperes.

The thermostats, which contain about 6 cubic feet of water each, are so lagged and heated that they would attain without automatic regulation a temperature too low by perhaps a degree. Electric heating by bare-wire helixes with alternating current at 30 volts, controlled by a toluol regulator, supplies the further heat needed. The temperature is thereby kept fluctuating about a mean, and the variations, of perhaps .005°, are so smoothed out by the heat capacity and imperfect conduction of the streams in the coils, as to keep these streams well within .001° of the desired temperature.

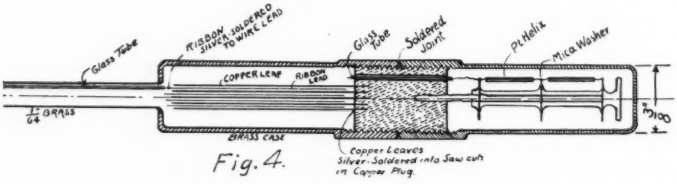

Fig. 4.

The regulators consist of about 60 feet of $\frac{1}{4}''$ copper tubing, closed at one end, the other terminating in the top of a piece of half-inch iron pipe 6″ long, capped at both ends. Through this top extends also a steel tube $\frac{1}{8}''$ diam., to near the bottom of the pipe, where it is amalgamated with mercury. All joints are soldered. Mercury fills the lower portion of the pipe; toluol the rest and all of the copper tube. When the toluol expands, mercury is forced up the steel tube into a glass capillary attached to its upper end, and there makes an electric contact which operates a relay and circuit-breaker, stopping the heating current or introducing resistance. The purpose of amalgamating the end of the steel tube is to keep the toluol from creeping. The success of these regulators, whose task is made severe by the flow of unthermostated water, is attributed to the close thermal contact of the toluol with the bath, to the large quantity of toluol used, giving ample sensitiveness, and to the generous size of the bath. No contact difficulties were experienced, and no drifting of temperatures noticed.

Although the coils of the thermal coupling were made as symmetrical as practicable, it was feared that when there was only a small quantity

of mercury present, any lack of complete symmetry might, by keeping the mercury from taking on the true mean temperature, affect the heat loss. A new coupling was therefore made, in which all of the outer turns were cold. This certainly resulted in a temperature distribution much more dependent upon the quantity of mercury present. No influence on the data was found. A separate test showed the heat loss from the Dewar flask to be so small that the entire contents of the flask might have changed in temperature by five degrees without affecting the final result, the 73° calorie, by one part in a thousand.

Two series of consecutive runs are given. A third series, taken between the other two, is omitted, having been taken with a different arrangement of the calorimeter, under unsteady conditions resulting therefrom. Of the first series only the results are given. The last, figures 5 to 10, is plotted in terms of the bridge readings. In this series it was attempted to obtain readings for two flows, with two temperature differences for each flow, resulting in four groups of points. No two points in any one group were taken in succession. The importance of this is shown especially in the data for figure 7, where the points scatter widely. Reference to the data shows this to be due not to erratic readings but to a gradual drift, leaving the result practically unaffected. Δ is given in centimeters of bridge wire, this unit being equivalent to about .016 degrees. The flows were 7.5 c.c./sec. and 15 c.c./sec., marked *s* and *f* respectively.

Data for figure 7.

Flow	Δ_0 + const.	Δ_2 cm.
s	19.93	132
s	9.77	570
f	7.33	577
f	17.85	90
f	8.29	514
s	9.90	512
s	17.14	163
s	9.24	520
f	8.66	492
f	17.61	92
s	16.25	169
s	8.92	529
s	16.70	176
f	17.77	100
f	8.31	503

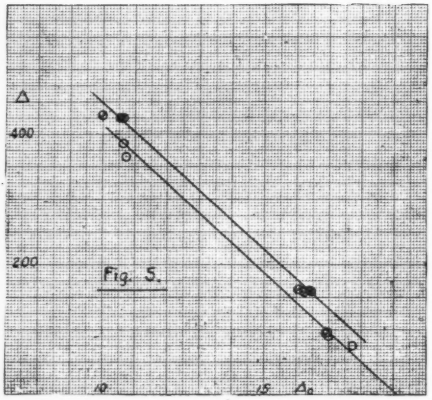

Fig. 5.

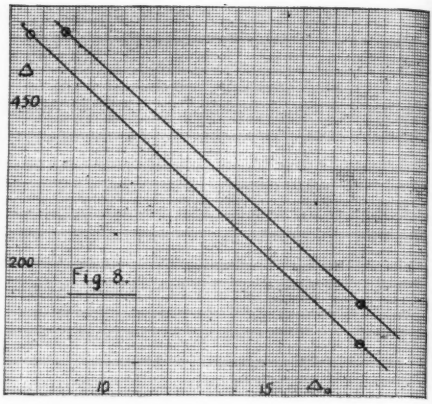

Fig. 8.

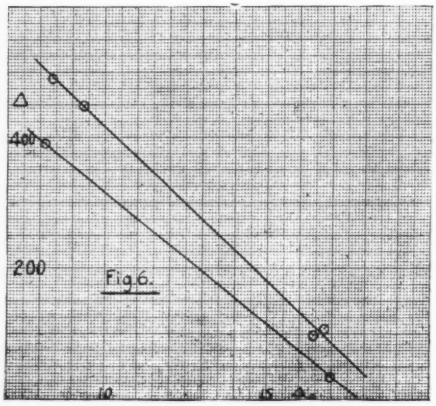

Fig. 6.

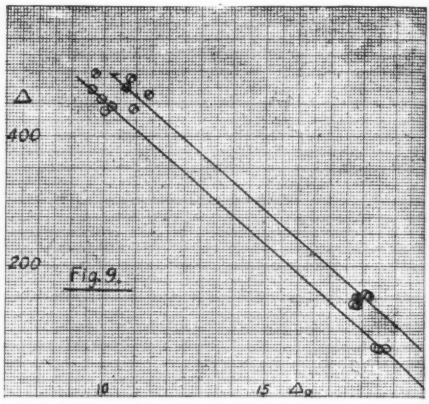

Fig. 9.

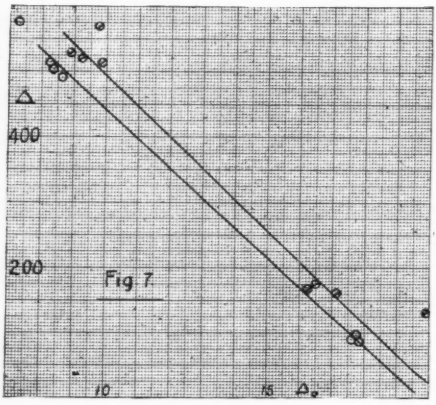

Fig. 7.

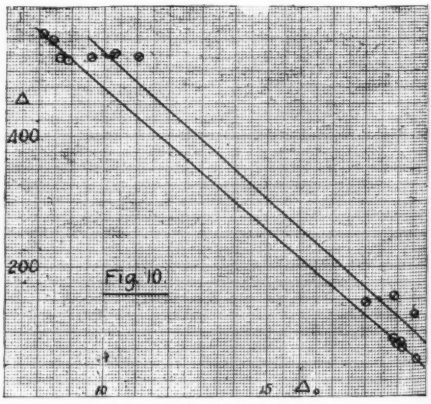

Fig. 10.

The first column of figures gives the difference between the two readings of a Carey Foster bridge. The second gives similar differences added to the small auxiliary resistances employed. These data are plotted in figure 7, using Δ_2 which was measured, instead of Δ_1. Correction for this is made by multiplying the slopes by $\frac{\Delta_2}{\Delta_1} = \frac{\Delta_2}{\Delta_2 - \Delta_0}$, which amounts to the addition of .0004 to the numerical values of the slopes. Thus corrected, these slopes are −.0219 for the slow flow, and −.0228 for the fast flow, giving −.0237 when the correction for B/f has been applied. A further correction is applied to reduce this result to the scale of a single thermometer,— it thus becomes −.0198, the value which appears in its proper place in the table below. The slopes have in all cases been obtained arithmetically, and may not be in exact agreement with the plotted lines.

In the following table, a "set" consists of at least four points,— one in each group. The first series of four runs, though comprising a considerable number of points, is not entitled to as much consideration as the last, because the points were not taken in regular order, and often lie too close together. If the last six runs alone be considered, and if they be weighted according to the number of sets in each run, the mean is −.0201, which perhaps best represents the data.

Number of sets in the run	$(c_2 - c_1)/c_2$
	−.0191
	.021
	.0189
	.0184
3	.0191
1	.0254
3	.0198
1	.0177
3	.0198
3	.0208

Had the previous data been included, counting each as a single set, they would have reduced the result by two parts in ten thousand. This figure needs but one further correction, that to the gas scale. For this purpose use was made of Callendar's well-known formula

$$t - pt = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100}$$

in which the quantity δ is as yet unknown. A thermometer calibrated by the Bureau of Standards at Washington was obtained, its δ being given as $1.47 \pm .01$. By comparison of the two, the δ of the thermometer in whose scale these results are given was found to be 1.53. This value, when put in the Callendar formula, gives as net corrections in the intervals of 17°–23° and 70°–76°, which were approximately the intervals used in the last series of runs, the values −0.055° and 0.042° respectively, increasing $c_2 - c_1/c_2$ from −0.0201 to −0.0040, whence the ratio of the specific heats c_1/c_2 is **1.0040**. In its relation to the results of previous observers this is shown by a circle on the 73° line of figure 1.

The average deviation from the mean, of the last six runs weighted as before, is 0.0007. The "probable error" is about 0.0003. The error arising from the reduction of thermometer ✱5 to ✱3 cannot well be greater than 0.0002. A larger error might have crept in through the δ correction. If this be due to an error of 4% in δ, the change in c_1/c_2 would be a little less than 0.0007. In this connection it is to be noted that the value 1.53 for δ is within about 4% of the lowest value ever found for platinum, and within 2% of the δ values commonly found. Since a decrease in δ would result in raising the point plotted in figure 1, no possible uncertainty in δ could raise that point above about 1.0047. If the "probable error," namely 0.0003, the estimated limit of error from the thermometer comparison, namely 0.0002, and the error due to a 2% uncertainty in δ, namely about 0.0003, be added, the total uncertainty in c_1/c_2 would be about 0.0008. The root mean square of these errors would be a little less than 0.0005.

It will be noted from figure 1 that the author's value, 1.0040, agrees very closely with Dietrici's and fairly closely with that of Barnes, which has been corroborated by Callendar. Bousfield's value, on the other hand, lies close to the older work of Lüdin and of Regnault, and the formula of Jager and von Steinwehr, if extrapolated from 50° to 73°, gives 1.0088, which happens to agree almost exactly with Bousfield. These results fall, therefore, quite definitely into two groups, one of which averages about half a percent higher than the other. Now it happens that all four of the methods that led to the high results involved the use of calorimeters containing a stationary pool of water with a free surface,[2] while of the four low values, three were obtained

[2] The methods of Janke, Cotty, and Bartoli and Stracciati are also of this type, and their results also run high.

by continuous flow calorimetry and one by the use of water hermetically sealed in quartz capsules. This difference may be significant. Unfortunately, however, although it suggests a number of possible explanations of the discrepancy, no one of them, when examined quantitatively, seems to give a correction term of the right order of magnitude.

Summary.

The work reported in this paper leads to the value

$$1.0040 \pm 0.0005$$

for the ratio of the specific heat of water at 73° C. to that at 20° C. This agrees more closely with the results of Dieterici, Barnes, and Callendar than with those of Regnault, Lüdin, Bousfield, and Jager and von Steinwehr.

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